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Chapter 5

Quantum Wells and Ultrathin Metallic Films

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Abstract

The chapter illustrates how simple quantum mechanics can sometimes provide quite precise description of nanophysics phenomena. From this perspective, both exact and approximate solutions for the bound-state energy of an electron in a square well are exposed. These results are used to improve the calculation of quantum size effects (QSEs) in ultrathin metallic films, obtained by several authors with simpler models of quantum wells. We show that, for a small (less than 5) number of monolayers, the differences between the predictions of these simpler models, and our approach, are important. Methods to improve the accuracy in the evaluation of various quantum size effects are shortly discussed. Using quantum mechanical-electromagnetic analogies, our results can be used in the study of light propagation in dielectric wave guides.

Keywords: ultrathin metallic films, quantum wells, finite square well, quantum size effects, heterojunctions

1. Introduction

If the dimension of a physical system is reduced, on one or several directions, up to the nanometric range, electron confinement generates states specific to quantum wells, quantum dots, or to other nanostructures, studied by new branches of science, nanophysics and nanotechnology, extremely interesting from both applicative and fundamental perspectives. A fascinating aspect of nanophysics is that it can be sometimes understood using elementary, one-particle quantum mechanics; for instance, many phenomena specific to quantum wells can be treated using the simple model of a particle in a rectangular potential.

A class of physical systems which can be studied in the frame of this model is a particular kind of quantum wells—the ultrathin metallic films. In the last decades, they were object for

active investigation, mainly due to the quantum size effects (QSEs), like the oscillatory behavior of the film stability [1], of the lattice deformation [2], of the work function [3], etc., in dependence of the number of atomic monolayers. The QSEs, predicted in the pioneering papers of Sandomirskii [4] and Schulte [5], are important for both practical and theoretical reasons. The ultrathin metallic films have a special relevance for ferromagnetic materials, as they are responsible for the giant magnetoresistivity of the Fe/Cr antiferromagnetic lattice [6]. Also, the possibility of obtaining ultrathin metallic films, having a specific number of monolayers, allows the experimentalist to tune the work function, controlling the chemistry of the metallic surface [3]. All these effects can be satisfactorily explained with a quite simple physics, whose basic ingredient is the different quantization imposed to electrons moving on longitudinal and transversal directions. Namely, the electrons moving parallel to the surface of the metallic film are quantized by cyclic conditions; the result is that the wave vectors are quasi-continuous. The electrons moving perpendicular to the film are considered as confined in a rectangular well, so they are quantized according to the theory of quantum wells; the result is that the spectrum is discrete.

How simple can the model of the well be, in order to provide a quantitative understanding of the physics of ultrathin metallic films? In spite of its simplicity, even the model of the infinite rectangular well gives sometimes good results, for instance, for the calculation of lattice deformation [2] or of Fermi energy [7]. These successes can be explained by the fact that, if the number of monolayers is not very small, $(n \gtrsim 25)$, the deep levels play a dominant role, and the difference between the corresponding levels (i.e., having the same quantum number) of the finite and of the infinite well is negligible. However, for a small number of monolayers $(n \lesssim 5)$, this approximation does not work anymore. This is why it is important to obtain the exact value of the energy levels in the finite well or at least a precise approximation.

In this chapter, we shall present exact or approximate analytic results for the energy levels of a finite square well and show how they can improve the simple theoretical models which give a quantitative understanding of the behavior of ultrathin metallic films, especially the QSEs. Its structure is the following: in the second section, we shall discuss the quantum problem of the finite square well, mainly in order to put the eigenvalue equations in an appropriate form. The next one is a short review of the various attempts of solving these transcendental eigenvalue equations. The fourth section describes a simple algebraic approximation of the solution of the eigenvalue equations—the parabolic approximation—mentioning also similar but more precise approaches. In the next one, we put the eigenvalue equations in differential form and obtain the exact solution as a series expansion. The sixth section is devoted to the applications in the quantum statistical physics of the ultrathin metallic films of the analytic results obtained for the bound-state energy in a finite square well. By analyzing the predictions of the three models frequently used in the physics of ultrathin metallic films (infinite, semi-infinite, and finite square well) for the Fermi wave vector, we show the key role played by the finitude of the well, in the evaluation of QSEs. In the last section, we describe how our results can improve the current theory of this class of metallic films.

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2. The bound states of a particle in a finite rectangular well

Until the mid-1980 of the previous century, the finite rectangular well was just an elementary problem of quantum mechanics, with applications in finding the energy levels of the quasi-free electrons on long molecules [8] or of the Ramsauer-Townsend effect [9]. The progress of solid-state physics, which finally led to the fabrication of quantum wells [10], quantum dots, or ultrathin metallic films [11, 12] and to the observation of QSEs associated with them, transformed these simple systems from problems of elementary quantum mechanics into theoretical models of devices of great practical interest.

We shall study now the movement of a particle in a finite rectangular well. There are, in principle, two ways of defining the potential of the well, choosing the origin of the energy $(E = 0)$ at the top or at the bottom of the well. In the first case, the advantage is that the energy of the bound states ("inside the well") is negative, as usual in quantum mechanics; in the second one, that is, in the limit of a very deep well, the energy level tends to the energy of the corresponding level of the infinite well. Even elementary, this distinction might be useful, in order to avoid confusions. We shall examine in detail the first case, so we shall consider a potential having the form (**Figure 1**):

$$V(x) = -U \cdot \theta\left(\frac{a}{2} - |x|\right) \tag{1}$$

where θ is the Heaviside function. The second case is shortly mentioned later on (Eqs. (24) and (25)). The Schroedinger equation for a particle of mass m moving in the potential (1) is

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) - E\right]\psi(x) = 0 \tag{2}$$

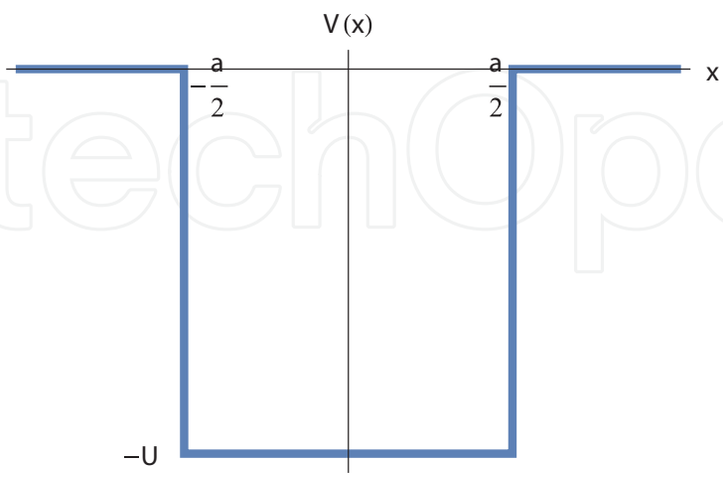

Figure 1. The square well potential (Eq. (1)).

As the potential is invariant at spatial inversion, $V(x) = V(-x)$, the solutions have well-defined parity. Let us put

$$E = -\frac{\hbar^2 \varkappa^2}{2m}, \quad U = \frac{\hbar^2 k_0^2}{2m}; \quad k^2 = k_0^2 - \varkappa^2 \tag{3}$$

where the quantities $k, k_0, \varkappa$ have the dimension of wave vectors. With these notations, the Schroedinger equation for the particle inside the well takes the form:

$$\left(\frac{d^2}{dx^2} + k^2\right)\psi(x) = 0, \quad |x| < \frac{a}{2} \tag{4}$$

For the particle outside the well, it is

$$\left(\frac{d^2}{dx^2} - \varkappa^2\right)\psi(x) = 0, \quad |x| > \frac{a}{2} \tag{5}$$

The even solutions are

$$\begin{aligned} u_+(x) &= A_+ \cos kx, & 0 \leqslant x \leqslant a/2 \\ u_+(x) &= A_+ \cos ka \;\; e^{\varkappa(a-x)}, & x > a/2 \\ & u_+(-x) = u_+(x) \end{aligned} \tag{6}$$

and the odd ones are

$$\begin{aligned} u_-(x) &= A_- \sin kx, & 0 \leqslant x \leqslant a/2 \\ u_-(x) &= A_- \sin ka \;\; e^{\varkappa(a-x)}, & x > a/2 \\ & u_-(-x) = u_-(x) \end{aligned} \tag{7}$$

The continuity of the derivative in $x = a/2$ gives, for even states

$$\tan\frac{ka}{2} = \frac{\varkappa}{k} \tag{8}$$

and for odd states

$$\cot\frac{ka}{2} = -\frac{\varkappa}{k} \tag{9}$$

Defining the dimensionless parameter

$$P = k_0 a/2 = \sqrt{2mU}\,\frac{a}{2\hbar} = \frac{1}{p} \tag{10}$$

sometimes called potential strength, which actually characterizes both the particle (m) and the well (a, U), Eqs. (8) and (9) become

$$\tan\frac{ka}{2}=\frac{\sqrt{k_0^2a^2-k^2a^2}}{ka}=\frac{\sqrt{P^2-k^2(a/2)^2}}{ka/2},\quad even\ \ states \tag{11}$$

$$\cot\frac{ka}{2}=-\frac{\sqrt{k_0^2a^2-k^2a^2}}{ka}=-\frac{\sqrt{P^2-k^2(a/2)^2}}{ka/2},\quad odd\ \ states \tag{12}$$

Also, the energy is

$$E=-U\left[1-\left(\frac{ka}{2P}\right)^2\right]\ \ //13 \tag{13}$$

Using well-known trigonometric identities, Eqs. (11) and (12) take the form:

$$\frac{\cos\frac{ka}{2}}{\frac{ka}{2}}=\pm\frac{1}{P}\ \ (even\ \ states);\quad \frac{\sin\frac{ka}{2}}{\frac{ka}{2}}=\pm\frac{1}{P}\ \ (odd\ \ states) \tag{14}$$

The sign must be chosen in agreement with Eqs. (11) and (12), so to satisfy the conditions $\tan\frac{ka}{2}>0$ for even states and <0 for odd states, as we shall indicate explicitly in the forthcoming paragraphs.

In other words, to solve the eigenvalue, Eq. (14) means to find the functions $\zeta(p),\ \xi(p)$, satisfying the equations:

$$\frac{\sin\zeta(p)}{\zeta(p)}=\pm p,\quad \frac{\cos\xi(p)}{\xi(p)}=\pm p,\quad p=\frac{1}{P} \tag{15}$$

This is, of course, a difficult task. If we write Eq. (15) in a slightly different form

$$\frac{\sin x}{x}=y(x),\quad \frac{\cos x}{x}=y(x) \tag{16}$$

to solve Eq. (15) means to invert the function $y(x)$ defined by Eq. (16), i.e., to obtain the function $x(y)$. Clearly, x in Eq. (16)—and in the rest of the chapter—has nothing to do with the space coordinate x, as initially used in Eqs. (1)–(7).

The functions $\zeta(p), \xi(p)$ correspond to the intersections of the plots of the functions $\sin x/x$, $\cos x/x$ with the line $y=\pm p$, which satisfy the sign rule mentioned, after Eq. (14). The number of solutions depends on the value of p. If there is at least one solution $\xi(p)$ for any p, the solution $\zeta(p)$ exists only for $p<1$. In **Figure 2**, the functions $\sin x/x$, $\cos x/x$ and the line $y=\pm p$, for $p=0.1$, are plotted. The $x-$coordinate of the intersections corresponds to the functions $\zeta(p), \xi(p)$, as we shall explain later on.

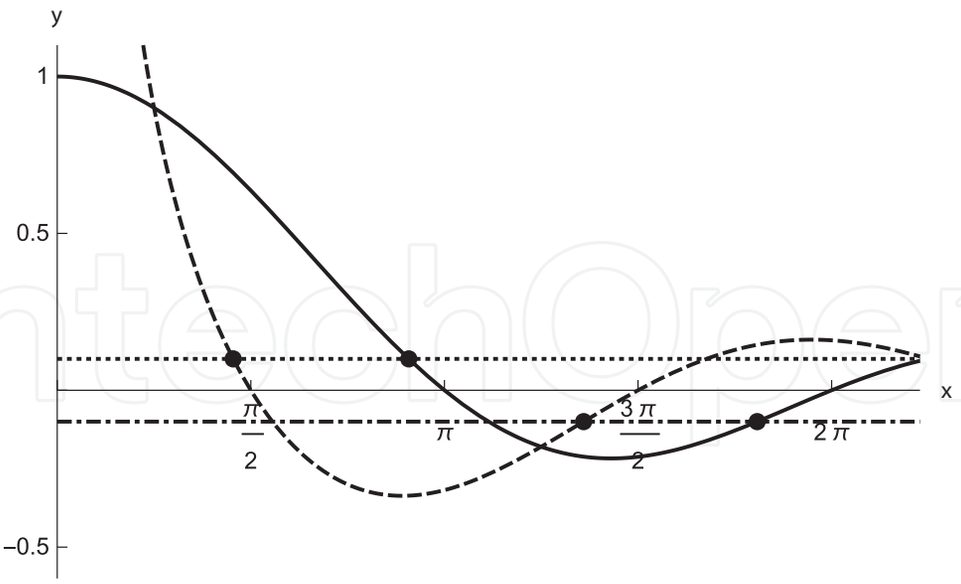

Figure 2. The $x-$ coordinate of the intersection points between the functions $\sin x/x$ (solid) and $\cos x/x$ (dashed) with the lines $y(x) = p$ (dots) and $y(x) = -p$ (dash-dots), marked with a point, corresponds to the functions $\zeta_1(p), \zeta_2(p),$ respectively, $\xi_1(p), \xi_2(p),$ for $p = 0.1$.

We shall write in a more explicit form Eq. (15), taking into account both the sign of the tan function (or of the cot function, which is, evidently, the same thing), as already mentioned, and the intervals of monotony of the functions $\sin x/x$, $\cos x/x$ [13]. The extremum points of the function $\cos x/x$ are given by the roots r_{cn} of the equation:

$$\tan x = -\frac{1}{x} \tag{17}$$

where r_{cn} is the root closest to $(n-1)\pi$. The eigenvalue equations for the even states are

$$x \in \left(0, \frac{\pi}{2}\right): \quad \frac{\cos x}{x} = p; \quad x \equiv \xi_1(p) \tag{18}$$

$$x \in \left(r_{c2}, \frac{3\pi}{2}\right): \quad \frac{\cos x}{x} = -p; \quad x \equiv \xi_2(p) \tag{19}$$

$$x \in \left(r_{c3}, \frac{5\pi}{2}\right): \quad \frac{\cos x}{x} = p; \quad x \equiv \xi_3(p) \tag{20}$$

and so on.

Similarly, the extremum points of the function $\sin x/x$ are the roots r_{sn} of the equation:

$$\tan x = x \tag{21}$$

where r_{sn} is the root closest to $\left(n - \frac{1}{2}\right)\pi$. The eigenvalue equations for the odd states are

$$x \in (r_{s,2}, 2\pi): \quad \frac{\sin x}{x} = -p; \quad x \equiv \zeta_2(p) \tag{22}$$

$$x \in (r_{s,3}, 3\pi): \quad \frac{\sin x}{x} = p; \quad x \equiv \zeta_3(p) \tag{23}$$

and so on. Each of Eqs. (18)–(20) and (22)–(23) has a unique solution, $\xi_1(p)$, $\xi_2(p)$, $\xi_3(p)$, respectively, $\zeta_2(p), \zeta_3(p)$. On the aforementioned intervals, the functions $\cos x/x$, $\sin x/x$ are monotonic and have an inverse. The inverse functions are $\xi_1(p)$, $\xi_2(p)$, $\xi_3(p)$, respectively, $\zeta_2(p)$, $\zeta_3(p)$. The function $\zeta_1(p)$ satisfies the equation:

$$x \in (0, \pi): \quad \frac{\sin x}{x} = p; \quad x \equiv \zeta_1(p) \tag{24}$$

According to Eq. (13), the energy eigenvalues are

$$E_n = -U + U\left(\frac{k_n a}{2P}\right)^2 \tag{25}$$

If the particle moves not in potential $V(x)$ given by (1), but in a potential

$$V^{(1)}(x) = V(x) + U \tag{26}$$

then the energy levels will be given by

$$E_n^{(1)} = U\left(\frac{k_n a}{2P}\right)^2 \tag{27}$$

According to the parity of n, $k_n a/2$ corresponds to the functions ξ and ζ, for instance, $k_1 a/2 = \xi_1(p), k_2 a/2 = \zeta_1(p),$ etc.

As already mentioned, the advantage of using the potential (1) is that the energy of a particle "inside the well," so in a bound state, is negative, corresponding to the most usual convention of quantum mechanics. However, the form (26) of the potential has the advantage that its levels approach, in the limit of a very deep well, the levels of the infinite well. Indeed, for $n \to \infty,$ so for very deep wells, the quantization condition for the wave vector becomes $k_n a \simeq n\pi,$ so

$$k_n \simeq \frac{n\pi}{a} \tag{28}$$

and Eq. (27) gives the expression of the wave vector corresponding to the $n-$th state in an infinite well:

$$E_n^{(\infty)} = \frac{\pi^2 \hbar^2}{2ma^2} n^2 \tag{29}$$

3. Solving the eigenvalue equation of the finite well: a historical perspective

The eigenvalue equations for the wave vectors (18)–(20) and (22)–(24) are transcendental equations, and their solutions cannot be written as a finite combination of elementary functions. More than this, till now, they cannot be expressed neither in terms of the special functions of the mathematical physics. There are a large number of papers devoted to this subject, in the last 60 years.

The first one, due to Pitkanen [14], writes the eigenvalue Eqs. (8) and (9) in the simpler form (18)–(20) and (22)–(24), providing an interesting visualization of the solutions. The second one, due to Cantrell [15] (who does not cite [14], producing a delay in the circulation of this paper), also proposes the replacement of Eqs. (8) and (9) with (18)–(20) and (22)–(24)—in fact, a repetition of Pitkanen's contribution—and notices that the eigenvalue equation for odd states is also the eigenvalue equation for a particle moving in a semi-infinite well, i.e., in a potential given by

$$U(x<0)=\infty, \quad U(0<x<a)=-U_0, \quad U(x>a)=0 \tag{30}$$

Graphical solutions are proposed by Guest [16], who made visible the similarities between the bound-state energies in a finite well and the modes of a metallic wave guide ([17]; fig. (8.14)); actually, both the electrodynamic and quantum mechanical problems are equivalent forms of the same Sturm-Liouville problem [18]. Aronstein and Stroud [19] wrote the eigenvalue equation as

$$\frac{ka}{2}+\arcsin\frac{ka/2}{P}=\frac{n\pi}{2} \tag{31}$$

This elegant form had been already given in the first edition of Landau's textbook of quantum mechanics, in the late 1940s of the twentieth century (for the English version of a more recent edition, see [20]) but remained unknown to Western physicists—a minor but significant consequence of the poor circulation of scientific information during the Cold War.

A completely different approach was proposed by Siewert [21], who obtained an exact solution in an integral form; unfortunately, it is very complicated and of limited practical use. Recently, Siewert's solutions were discussed in the context of generalized Lambert functions [22], a subject under intense investigation.

Among the papers which provide approximate analytical solutions of the eigenvalue Eqs. (18)–(20) and (22)–(24), the most popular one, authored by Barker et al. [23], is essentially a low-order algebraic approximation of $\sin x, \quad \cos x$. Another interesting contribution is that of Garrett [24], who introduced an intuitive physical concept, the characteristic depth δ of a finite well, for a bound electron with energy E:

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$$\delta = \frac{\hbar}{(2m(V_0 - E))^{1/2}} \quad /32 \tag{32}$$

as the magnitude of the domain outside the well, where the wave function can penetrate significantly, decreasing however exponentially. This concept is similar to the concept of skin depth in electromagnetism [17] or to the concept of viscous penetration depth in fluids [25], § 24.

In the context of various approximations, it is worth to mention the "algebraization" of trigonometric functions, proposed by de Alcantara Bonfim and Griffiths [26], which transforms the transcendental equations for the eigenvalues of the finite well in approximate, tractable, algebraic equations. For instance, we can use the approximations:

$$\tan x \simeq \frac{0.45x}{1 - \frac{2x}{\pi}}; \quad \cos x \simeq \frac{1 - (2x/\pi)^2}{(1 + cx^2)^s}, \quad 0 \leqslant x \leqslant \frac{\pi}{2} \tag{33}$$

where the pair of constants can be chosen as

$$s = 1/2, \quad c = 0.212 \text{ or } s = 1, \quad c = 0.101 \tag{34}$$

4. The parabolic approximation

To solve the eigenvalue equations, or—more generally—Eq. (16), with $y \gtrless 0$, means, as already mentioned, to obtain the inverse of the function $y(x)$ defined by (16), i.e., to obtain the function $x(y)$. Geometrically, the inverse of the function $y(x)$, plotted as a curve whose generic point is (x, y), is its symmetric with respect of the first bisectrix. A generic point of the inverse function has the coordinates (y, x).

Clearly, only the monotonic functions can be inverted; for instance, in our case, the function $\sin x/x$ must be replaced with its restriction on their intervals of monotony, and this restriction will be actually inverted. We shall consider $r_{sn} \simeq \left(n - \frac{1}{2}\right)\pi$ and approximate the bump of the function $\sin x/x$ on the interval $(2n\pi, (2n+1)\pi)$ with a segment of parabola. It is easy to see that the ascendant part of this parabola is given by the equation:

$$y = \frac{4}{\left(2n + \frac{1}{2}\right)\pi^3}\left\{\frac{\pi^2}{4} - \left[x - \left(2n + \frac{1}{2}\right)\pi\right]^2\right\}, \tag{35}$$

$$2n\pi < x < \left(2n + \frac{1}{2}\right)\pi$$

Solving this equation for y

$$x = \left(2n + \frac{1}{2}\right)\pi - \sqrt{\frac{\pi^2}{4} - \frac{y}{4}\left(2n + \frac{1}{2}\right)\pi^3} \tag{36}$$

and making the change $x \leftrightarrow y$, we get for the root ζ_{2n} [27]:

$$\zeta_{2n}^{(par)}(x) = \left(2n + \frac{1}{2}\right)\pi - \sqrt{\frac{\pi^2}{4} - \frac{x}{4}\left(2n + \frac{1}{2}\right)\pi^3}, \tag{37}$$

$$0 < x < \frac{1}{\left(2n + \frac{1}{2}\right)\pi}$$

Following exactly the same steps, similar expressions can be obtained for $\zeta_{2n}(x < 0)$ and for all the functions ζ_q, ξ_q their parabolic approximations can be obtained. A special case is ζ_1 :

$$\zeta_{2n}^{(par)}(x) = \pi\sqrt{1 - x} \tag{38}$$

The method cannot be applied, evidently, for ξ_1, as the function to be inverted has no bump.

The explicit expressions of the parabolic approximation for the functions $\xi_n \ (n > 1)$ and ζ_n, obtained in [27] are simple, but cumbersome, and will not be given here.

It is possible to improve the parabolic approximation in two ways:

(1) To express the numerical coefficients in formulas similar to Eq. (36) using analytic approximations for the roots of the equations $\tan x = x$ and $\tan x = -1/x$. Actually, these transcendental equations can be transformed in approximate, tractable, algebraic equations, using the algebraic approximations of the tan function, proposed by de Alcantara Bonfim and Griffiths [26] and generalized by other authors [28]. This approach is sometimes called "improved parabolic approximation."

(2) To approximate the bumps of the functions $\sin x/x$ and $\cos x/x$ with a cubic curve (polynomial); this approach is sometimes called cubic approximation. The calculations are elementary, but cumbersome, and will not be given here [29].

For an algebraic approximation of ζ_1, we can use a formula similar to the cos approximation in Eq. (34), namely,

$$\frac{\sin x}{x} \simeq \frac{1 - \left(\frac{x}{\pi}\right)^2}{\sqrt{1 + 0.2x^2}} \tag{39}$$

proposed in [30].

The finite square well is a good starting point for similar quantum mechanical problems, i.e., the asymmetric well (when the walls of the well, see **Figure 1**, have different heights), the

semi-infinite well (when one of the walls is infinite), or more realistic cases, when the walls are rounded (see [11, 12]). These potentials can model a semiconductor heterojunction (a thin semiconductor slice sandwiched between two different, larger semiconductors), a metallic film deposited on a semiconductor (in vacuum), and so on.

5. The differential form of transcendental equations

We shall indicate now an approach for solving the eigenvalue Eqs. (18)–(20) and (22)–(24) providing an exact solution, written as a series expansion. We shall first illustrate this method with the function $\zeta_1(p)$.

Taking the derivative with respect to p in both sides of the equation

$$p\zeta_1(p) = \sin\zeta_1(p) \tag{40}$$

we get

$$\frac{d\zeta_1(p)}{dp} = \frac{\zeta_1(p)}{\cos\zeta_1(p) - p} \tag{41}$$

Using Eq. (40) and taking into account that we are in the second quadrant

$$\cos\zeta_1(p) = -\sqrt{1 - p^2\zeta_1(p)^2} \tag{42}$$

we obtain the differential form of the equation for $\zeta_1(p)$:

$$\frac{d\zeta_1(p)}{dp} = -\frac{\zeta_1(p)}{\sqrt{1 - p^2\zeta_1(p)^2} + p}, \quad p \in [0, 1], \quad \zeta_1(p) \in \left(\frac{\pi}{2}, \pi\right) \tag{43}$$

with the initial condition:

$$\zeta_1(0) = \pi \tag{44}$$

Putting

$$X_{2n}(p) = \zeta_n(p), X_{2n-1}(p) = \xi_n(p), \quad n = 1, 2, \ldots, \tag{45}$$

replacing p by x and relaxing the restriction $p > 0$, the equations for the eigenvalues of the wave vectors can be written in a unitary form:

$$\frac{dX_n(x)}{dx} = -\frac{X_n(x)}{\sqrt{1 - x^2X_n(x)^2} + x} \tag{46}$$

with the initial condition:

$$X_n(0) = \frac{n\pi}{2} \tag{47}$$

With Eq. (46), we can obtain the derivatives of any order of $X_n(x)$ in an arbitrary point x_0 and, consequently, write down the Taylor series for this function, with arbitrary accuracy. Choosing $x_0 = 0$, we get the following series expansion for $X_n(x)$:

$$X_n(x) = \sum_{m=0}^{\infty} q_m\left(\frac{n\pi}{2}\right)x^m \tag{48}$$

The parameters q_m are polynomials in the variable

$$\frac{n\pi}{2} \equiv b : \tag{49}$$

$$q_0(b) = b, \quad q_1(b) = -b, \quad q_2(b) = b \tag{50}$$

$$q_3(b) = -b\left(1 + \frac{b^2}{6}\right), \quad q_4(b) = b\left(1 + \frac{2b^2}{3}\right) \tag{51}$$

$$q_5(b) = -b\left(1 + \frac{5}{3}b^2 + \frac{3}{2^3 \cdot 5}b^4\right), \quad q_6(b) = b\left(1 + \frac{2 \cdot 5}{3}b^2 + \frac{2^3}{3 \cdot 5}b^4\right) \tag{52}$$

and so on. For the explicit expression of $q_m(b),\ m < 17,$ see [13]. The first three terms correspond to the Barker approximation.

Let us also remark that, in spite of the fact that the equivalence of Sturm-Liouville problems for electromagnetic fields and for wave functions was noticed many years ago, the results obtained for the finite rectangular well remain unused by the researchers studying wave propagation in wave guides or in other simple geometries. Reciprocally, the very detailed solutions of the equations for the normal modes of electromagnetic waves (see, for instance, the references [90, 92] in [31]) were apparently overlooked by researchers working in quantum mechanics.

6. Applications to the statistical physics of ultrathin metallic films

With few exceptions, the physics of ultrathin metallic films can be satisfactorily explained using different types of infinite well for the potential of electrons moving normally to the film plane. The model of the infinite well can be improved, for instance, by the phase accumulation theory [11, 12, 32], quite popular among the scientist working in surface physics. The theory

satisfactorily explains the quantum scale effects (QSEs) appearing in such systems and predicted theoretically in the pioneering papers of Sandomirskii [4] and Schulte [5].

If, for thin films, such theoretical models can be successfully applied, for ultrathin films, with only few (typically, less than 5) monolayers, obtained experimentally in the last two decades, the approximation of the infinite well is inadequate. This is why in such cases we have to use the exact solutions for the bound-state energy of the finite well or, at least, their analytic approximations. In order to make clear the differences between the predictions of the two models—the first one is based on the infinite well, and the second one is based on the finite well—we shall evaluate some QSE for an ultrathin metallic film for three potentials: infinite, semi-infinite, and finite wells.

6.1. The infinite well model for the quantum well in an ultrathin metallic film

Let us consider a rectangular metallic films, with edges $L_x, L_y, L_z,$ where L_x, L_y are macroscopic or mesoscopic and L_z is nanoscopic. If the metallic film is placed between two semi-infinite dielectrics, we can presume that the conduction electrons move freely in the plane of the film (defined by the axes Ox, Oy), and in transversal direction (Oz), the potential can be approximated by an infinite rectangular well. The film has the volume:

$$V = L_x L_y L_z \tag{53}$$

and the electron energy is

$$\frac{\hbar^2 \vec{k}^2}{2m} \tag{54}$$

where we put

$$\vec{k} = (k_x, k_y, k_z) = \left(\frac{2\pi}{L_x} n_x, \quad \frac{2\pi}{L_y} n_y, \quad \frac{\pi}{L_z} n_z\right) \tag{55}$$

$$n_x, \ n_y = \pm 1, \ \pm 2, \ \ldots; \ n_z = 1, \ 2, \ \ldots \tag{56}$$

The differences between the values taken by the integers n_x, n_y and n_z are due to the fact that, along the directions Ox and Oy, the quantization is obtained imposing cyclic conditions, and along the direction Oz by "rigid wall" conditions, specific to the infinite well, with impenetrable walls.

For ultrathin films, the discrete spectrum of k_z can be easily observed experimentally, and the conduction electrons constitute a quasi-2D multiband electron gas, characterized by a quasi-continuum, 2D wave vector $\vec{k}_{2D} = (k_x, k_y)$ and by a quantized wave vector $k_z = n_z \frac{\pi}{L_z}$.

The number $n_z = q$ plays the role of an subband index. So, in the 3D reciprocal space, the spectrum is formed by planes of allowed states (subbands), parallel to the xOy plane, and separated along the z direction, by segments of length $\Delta k_z = \pi / L_z$.

Let us consider a numeric example. For a metallic film with two atomic monolayers, the typical values are $L_z \sim 0.6\ nm,$ so $\Delta k_z \sim 5\ nm^{-1}$ and $k_F = 16\ nm^{-1}$. Therefore, only three plans cut the Fermi (hemi-)sphere, or—in other words—only the first subbands are occupied, corresponding to $p = 1, 2, 3$. Let us mention that there is no band corresponding to $p = 0,$ as, in this case, the amplitude of the wave function would be zero.

We shall compute the number of occupied electronic states and the Fermi wave vector of the ultrathin film. The total number of subbands, which cut the Fermi sphere is $Q,$ defined by

$$Q = \text{int}\left[\frac{k_F}{\Delta k_z}\right] \tag{57}$$

where int$[x]$ is the largest integer smaller than x. In our particular case, discussed in the previous example, $Q = 3,$ so there are only three distinct subbands, occupied at $T = 0$. For films with few monolayers, the subbands are separated by energies of about $1\ eV$, so we can consider that $T = 0$.

As the occupied states belonging to the subband of index q are situated inside circles cut by the Fermi sphere, of radius $k_{F,q} = \left[k_F^2 - (q\Delta k_z)^2\right]^{1/2}$ (these circles are the intersection of the subband plane with the Fermi sphere), and the area corresponding to one electronic state k in each subband is $(2\pi)^2 / L_x L_y = (2\pi)^2 L_z / V,$ there are

$$\frac{\pi k_{F,q}^2}{(2\pi)^2 L_z / V} = \frac{V}{(2\pi)^2 L_z} \pi k_{F,q}^2 \tag{58}$$

occupied states in the subband q. The number of electrons N inside the Fermi sphere is obtained by summing up over the occupied subbands:

$$N = 2\frac{V}{(2\pi)^2 L_z} \pi \sum_{q=1}^{Q} k_{F,q}^2 \tag{59}$$

$$= \frac{V}{2\pi L_z}\left[Qk_F^2 - \left(\frac{\pi}{L_z}\right)^2 \sum_{q=1}^{Q} q^2\right]$$

where the factor of 2 is due to the electron spin. Putting

$$\Sigma_1(Q) = \sum_{q=1}^{Q} q^2 = \frac{1}{6} Q(Q+1)(2Q+1) \tag{60}$$

and introducing the number density of electrons $n = N/V,$ we get

$$\left[k_F^2\right]_Q = n\frac{2\pi L_z}{Q} + \left(\frac{\pi}{L_z}\right)^2 \frac{\Sigma_1(Q)}{Q} \tag{61}$$

giving the dependence of the Fermi wave vector on the thickness L_z, on the number of subbands Q, and on the electron number density n.

Introducing Eq. (61) in Eq. (57), we get

$$\left[\frac{\pi}{12}Q(4Q+1)(Q-1)\right]^{1/3}\frac{1}{n^{1/3}} \leqslant L_z < \left[\frac{\pi}{12}Q(4Q+5)(Q+1)\right]^{1/3}\frac{1}{n^{1/3}} \tag{62}$$

The last two equations define the QSEs on the Fermi wave vector; they can be considered as the starting point of all other similar QSEs of various physical quantities characterizing the ultrathin film.

Choosing $n = 4 \cdot 10^{22} cm^{-3} = 40\ \ nm^{-3},$ we get the expression of the Fermi wave vector for an electronic gas 1, 2, 3, or 4 subbands:

$$\left[k_F^2\right]_1 = 80\pi L_z + \left(\frac{\pi}{L_z}\right)^2, \quad L_z < 0.5\ nm \tag{63}$$

$$\left[k_F^2\right]_2 = 40\pi L_z + \frac{5}{2}\left(\frac{\pi}{L_z}\right)^2, \quad 0.5\ nm \leqslant L_z < 0.8\ nm \tag{64}$$

$$\left[k_F^2\right]_3 = \frac{80\pi}{3}L_z + \frac{14}{3}\left(\frac{\pi}{L_z}\right)^2, \quad 0.8\ nm \leqslant L_z < 1.1024\ nm \tag{65}$$

$$\left[k_F^2\right]_4 = 20\pi L_z + 7.5 \cdot \left(\frac{\pi}{L_z}\right)^2, \quad 1.1024\ nm \leqslant L_z < 1.4006\ nm \tag{66}$$

where k_F is measured in nm^{-1}. The expressions (63)–(66) clearly illustrate the QSE on the Fermi wave vector.

6.2. The semi-infinite well model for the quantum well in an ultrathin metallic film

As already mentioned (see Eq. (45) and the remark just below Eq. (27)), the relation between the solutions of the eigenvalue Eq. (46), namely, the functions $X,$ and the wave vector k is

$$k \to \frac{2}{L}X \tag{67}$$

and the bound states of the semi-infinite well are described by the odd states of a finite well with the same length. In other words

$$k_{2n} \to \frac{2}{L_z}\zeta_n(p) \tag{68}$$

It is convenient to define

$$w = \left(\frac{mU}{2\hbar^2}\right)^{1/2} \tag{69}$$

So, the inverse strength of the quantum well, similar to Eq. (10), can be defined as

$$p = \frac{1}{wL_z} \tag{70}$$

According to Eq. (68), the wave vector depends on both L_z and U (or w). As U is a material dependent quantity, related, in principle, to the work function, we shall replace it, for this numerical example, with the typical value of $U = 5\ \ eV;$ in this case, Eq. (70) gives

$$p = \frac{1}{6.5 \times \overline{L_z}} \tag{71}$$

with $\overline{L_z}$ in nanometers.

An important difference which occurs at semi-infinite wells, compared to the infinite wells, is that it keeps a finite number of bound states. Consequently, the energy spectrum of the electron gas of the metallic film contains a finite number of subbands, in dependence of the value of p. The well keeps at least one state if

$$p < 1 \ \ \Rightarrow \overline{L_z} > \frac{1}{6.3} = 0.16\ \ nm \tag{72}$$

and exactly one state ζ_1 if

$$\frac{2}{3\pi} = 0.21221 < p < 1, \ \ or \ \ 0.16\ \ nm < \overline{L_z} < 0.74794\ \ nm \tag{73}$$

This corresponds, usually, to a film with one or two monolayers. We have two states in the well, ζ_1 and ζ_2, if

$$\frac{2}{5\pi} = 0.12732 < p < 1, \ \ or \ \ 0.16\ \ nm < \overline{L_z} < 1.2467\ \ nm \tag{74}$$

This corresponds, usually, to a film with up to four monolayers, etc. These conditions are purely mathematical, i.e., consequences of the specific form of the eigenvalue equations.

Now, we shall impose physical conditions, due to the $p-$ or $\overline{L_z}-$ dependence of the Fermi wave vector and of the number of subbands. Taking into account Eq. (67) and using an argument similar to Eq. (57), we find

$$k_F^2 = \frac{2\pi L_z}{Q} n + \frac{1}{Q}\left(\frac{2}{L_z}\right)^2 \sum_{q=1}^{Q} \left(\zeta_q(p)\right)^2 \tag{75}$$

Let us presume that the electron gas contains exactly Q subbands, which is equivalent to the relation:

$$\frac{2}{(Q-1/2)\pi} < p = \frac{1}{6.5 \times \overline{L_z}} < 1, \ \ or \ \ 0.16 \ \ nm < \overline{L_z} < 1.2467 \ \ nm \tag{76}$$

or

$$\frac{1}{6.5} < \overline{L_z} < \frac{(Q-1/2)\pi}{13} \tag{77}$$

Therefore, instead of Eq. (62), we have

$$\left(\frac{2}{L_z}\right)^2 \zeta_Q^2(p) \leqslant k_F^2 = \frac{2\pi L_z}{Q} n + \frac{1}{Q}\left(\frac{2}{L_z}\right)^2 \sum_{q=1}^{Q} \left(\zeta_q(p)\right)^2 \ \ //78 \tag{78}$$

The term corresponding to the r.h.s. of the inequality (62) is missing in this case, as the number of roots (solutions) is completely determined by the condition imposed to L_z, according to Eq. (77).

Replacing the electron number density with a typical value $n = 40\ nm^{-3}$ and using Eq. (63), we get (we took advantage of the fact that, incidentally, the numeric factor is $0.25128 \simeq 1/4$)

$$\zeta_Q^2(p) \leqslant \frac{1}{4Qp^3} + \frac{1}{Q}\sum_{q=1}^{Q} \left(\zeta_q(p)\right)^2 \tag{79}$$

This restriction on p, which can be verified using, for instance, the cubic approximation for ζ_n, must be considered together with Eqs. (71)–(73).

6.2.1. The finite well model for the quantum well in an ultrathin metallic film

The situation is quite similar to the previous one—the semi-infinite well. However, in this case, there is at least a solution for each value of p. Eqs. (71)–(73) are replaced by

$$p > 1 \ \ or \ \ \overline{L_z} < \frac{1}{6.3} = 0.16 \ \ nm, \tag{80}$$

$$\text{one state,} \ \ X_1 = \xi_1;$$

$$\frac{1}{\pi} = 0.31831 < p, \ \ or \ \ \overline{L_z} < 0.31831 \ \ nm, \tag{81}$$

$$\text{two states,} \quad X_1 = \xi_1, \quad X_2 = \zeta_1$$

$$\frac{2}{3\pi} = 0.21221 < p < 1, \quad or \quad \overline{L_z} < 0.74794 \ \ nm, \tag{82}$$

$$\text{three states,} \quad X_1 = \xi_1, \quad X_2 = \zeta_1, \quad X_3 = \xi_2$$

and so on. In Eqs. (76) and (77), the replacement $\zeta_q \to X_q$ must be done. Eq. (74), with $\zeta_q \to X_q$, gives the QSE for the Fermi wave vector.

These solutions, or their analytic approximations (for instance, the cubic one), can be used directly in the models already proposed for the infinite well [33], in order to obtain the electron density, the surface free energy, the surface dipolar moment, or other similar quantities, in the more realistic case of a finite rectangular well.

7. Conclusions

This chapter illustrates how solutions of a simple quantum mechanical problem can be used for the description of certain interesting phenomena of nanophysics. Specifically, we referred to the exact solutions of the eigenvalue equations for the eigenenergy of the bound states of a particle in a rectangular well. If the physical problem is elementary, and the wave functions are simply written in terms of elementary functions, the equations for the eigenvalues of energy (or of the wave vector) are transcendental—and highly nontrivial. We obtain both exact solutions (series expansions) of these transcendental equations and approximate ones—with various degrees of complexity and accuracy. The value of the Fermi wave vector of the electrons in the metallic film, calculated for the finite well model, differs drastically from those calculated with the infinite well one.

Our results for the one-electron wave functions of the finite barrier model can be used as Kohn-Sham state in the self-consistent calculations of surface energy [34], for more accurate calculations of the stability of the films [1] and of other QSEs [33]. They can be also used as zero-order approximations for more realistic potentials, e.g., with rounded walls or undulate bottom—in a Rayleigh-Schroedinger or Dalgarno-Lewis perturbation theory [35].

Using the analogy between the movement of electrons in time-independent potentials and propagation of electromagnetic waves in dielectrics or metallic wave guides [18], mathematically, they are identical Sturm-Liouville problems; our results can be extended to several problems of electromagnetism and optics. This analogy can be easily developed for planar dielectric waveguides, namely, for "step-index" dielectrics, consisting of a slab of higher refractive index (core), sandwiched between two half spaces of lower refractive index (cladding). In such a situation, the quantum counterpart of the dielectric guide is a square well. This issue is discussed in detail by Casey and Panish in the context of heterostructure lasers [36]. It is easy to notice that the eigenvalue equations for transverse electric and magnetic modes, (2.4–45, 54, 60, 66) in [36], are essentially identical with our Eqs. (8) and (9).

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